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(54) **PROTECTIVE STRUCTURE AND ELECTRONIC DEVICE WITH THE SAME**

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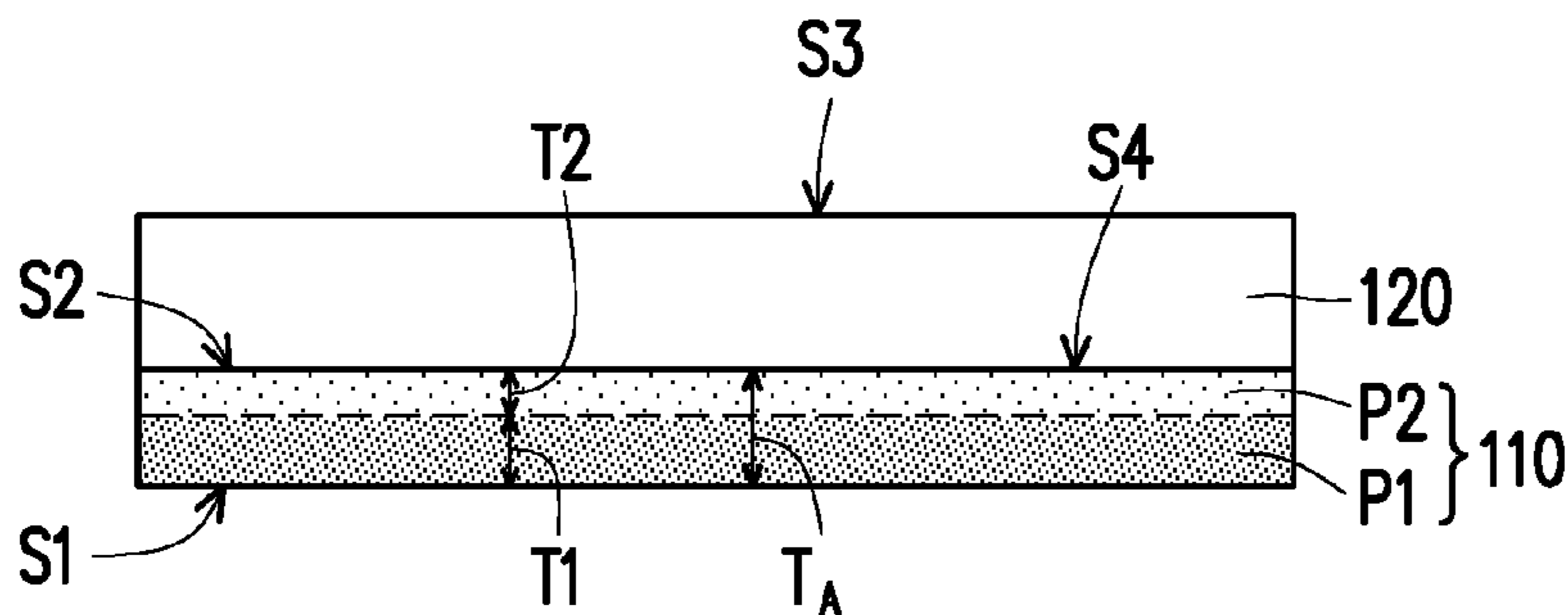
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(57) **ABSTRACT**

Provided is a protective structure including an auxiliary layer and a hard coating layer. The auxiliary layer has a first surface and a second surface opposite to the first surface. The hard coating layer is located on the second surface of the auxiliary layer. The Young’s modulus of the auxiliary layer is gradually increased from the second surface to the first surface. An electronic device with the same is also provided.

8 Claims, 7 Drawing Sheets



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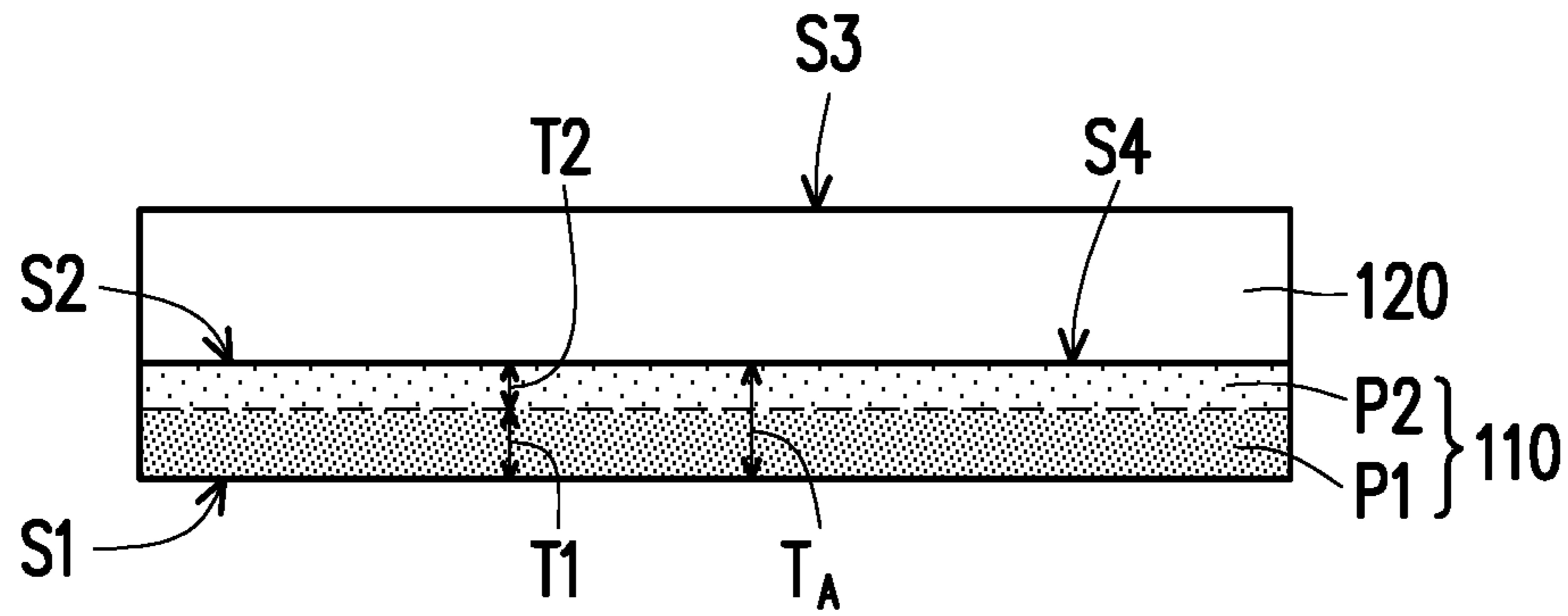
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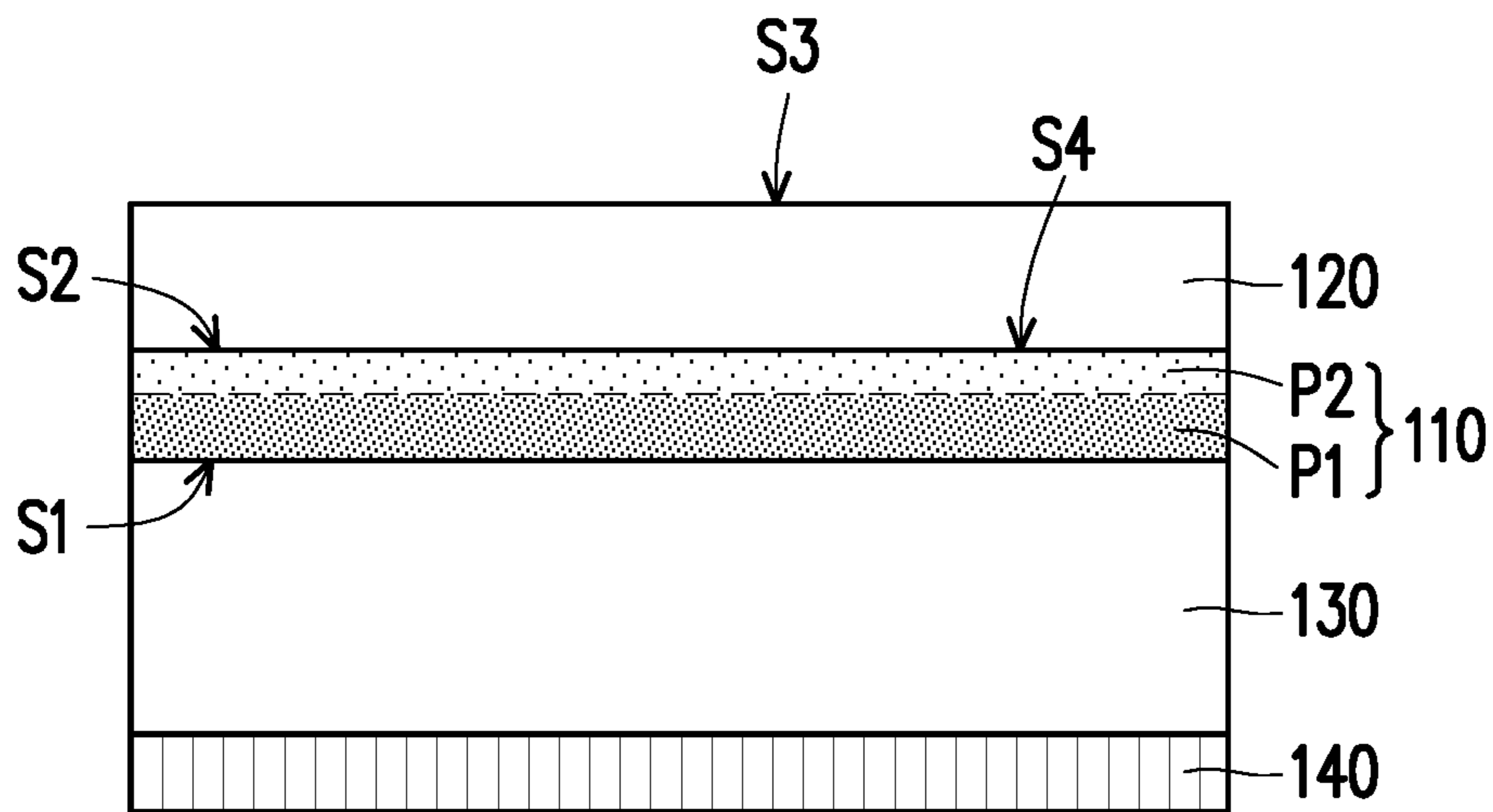
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100a

FIG. 1A



100b

FIG. 1B

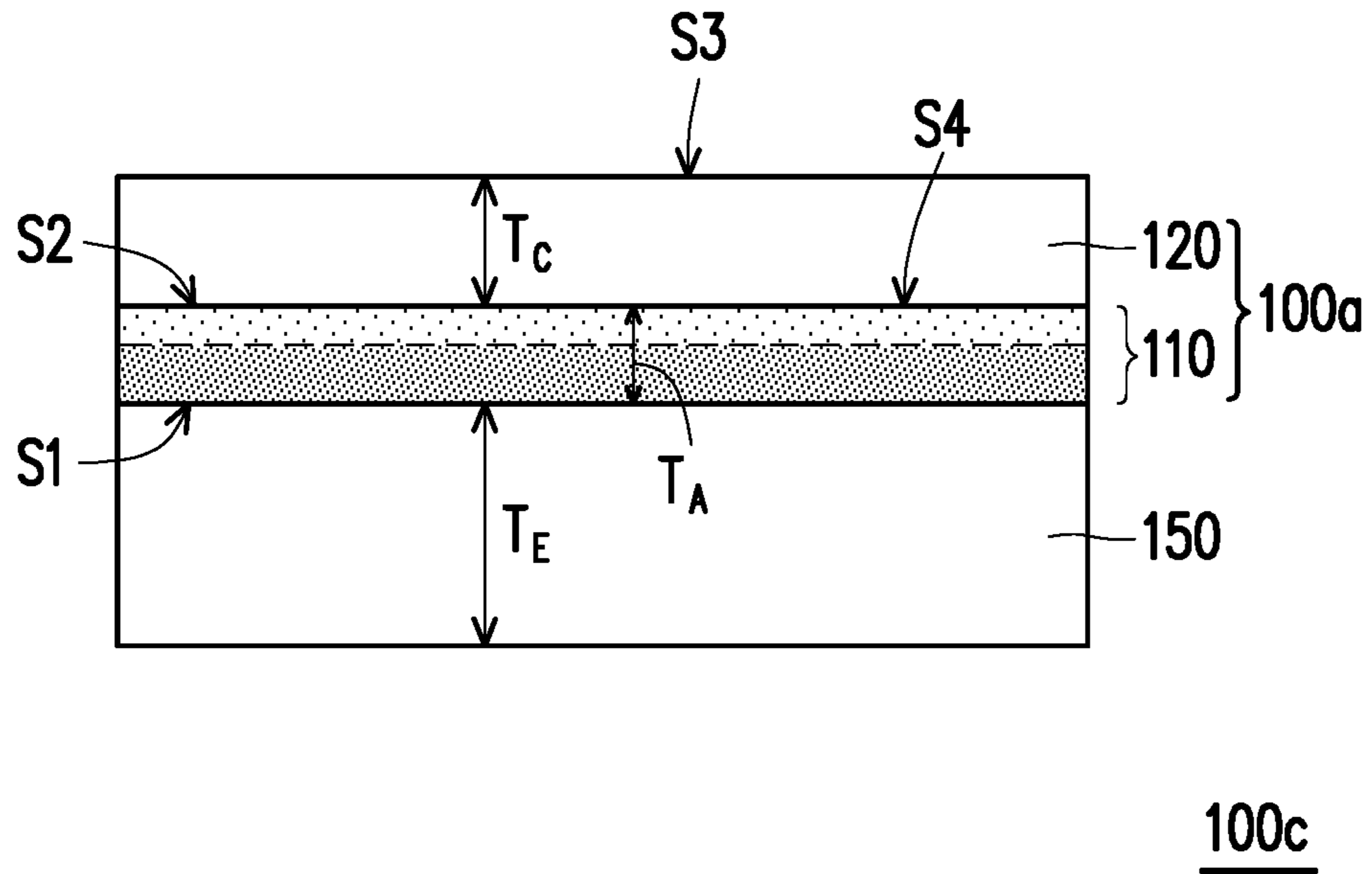


FIG. 1C

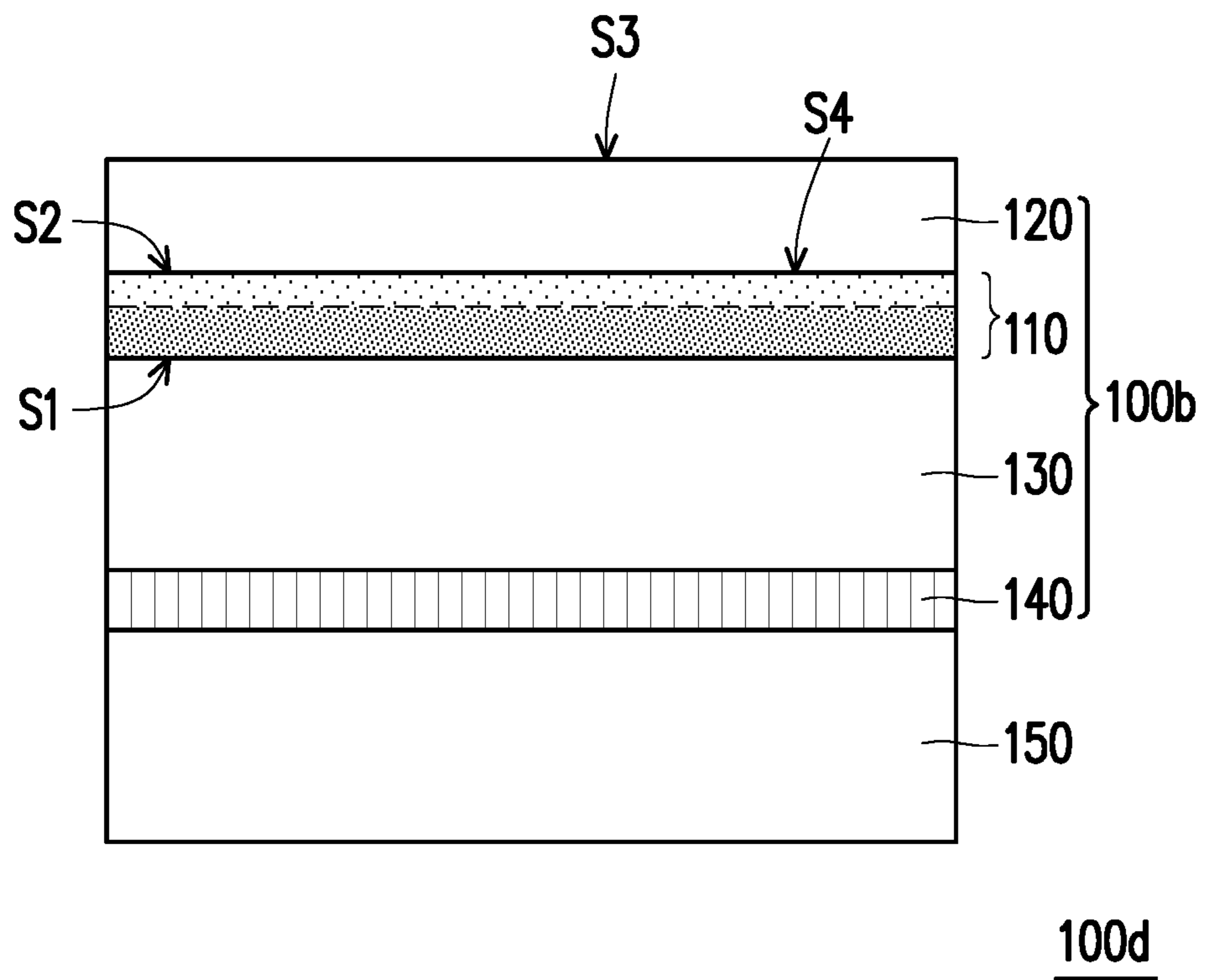


FIG. 1D

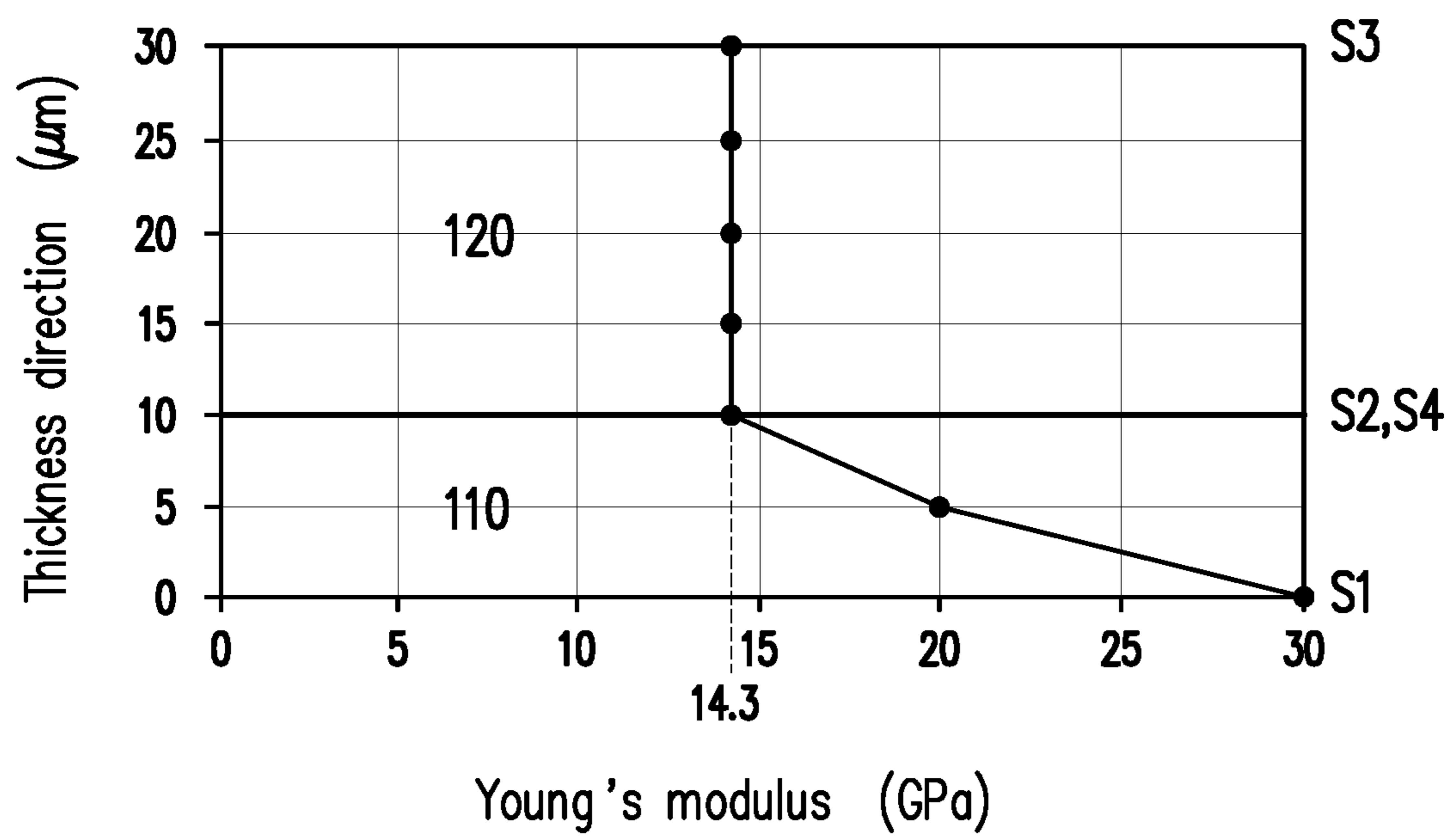


FIG. 1E

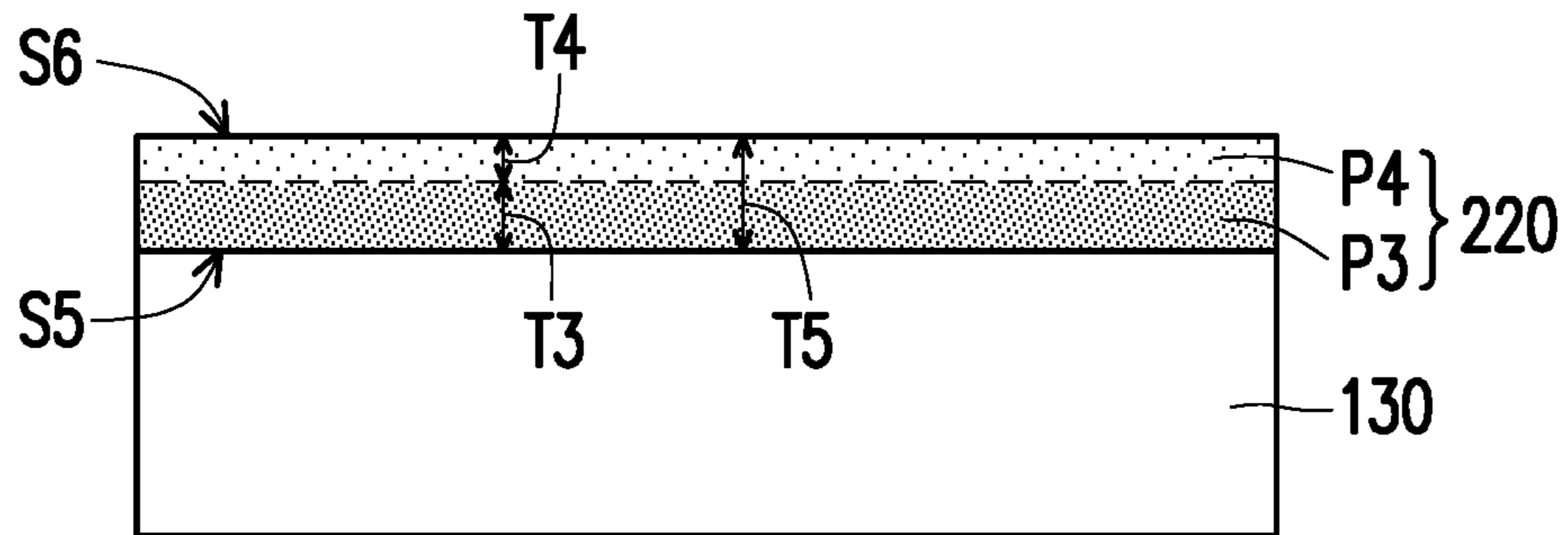


FIG. 2A

200a

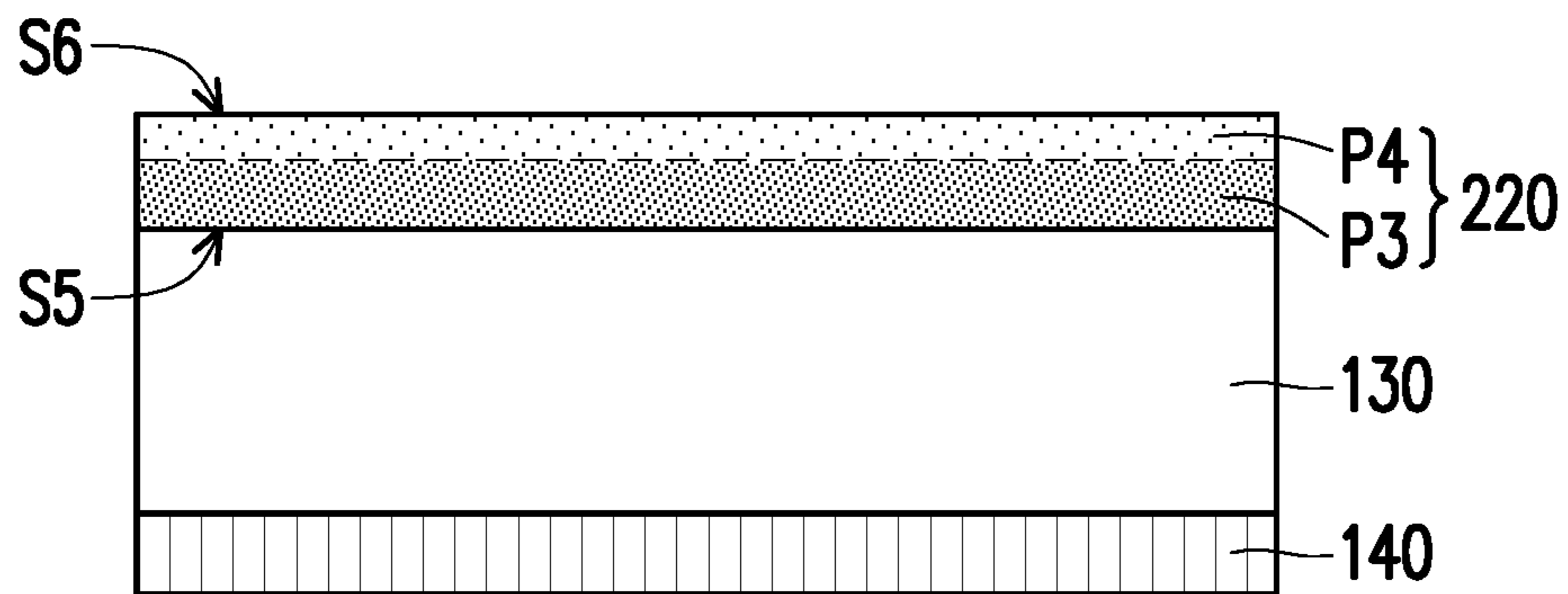


FIG. 2B

200b

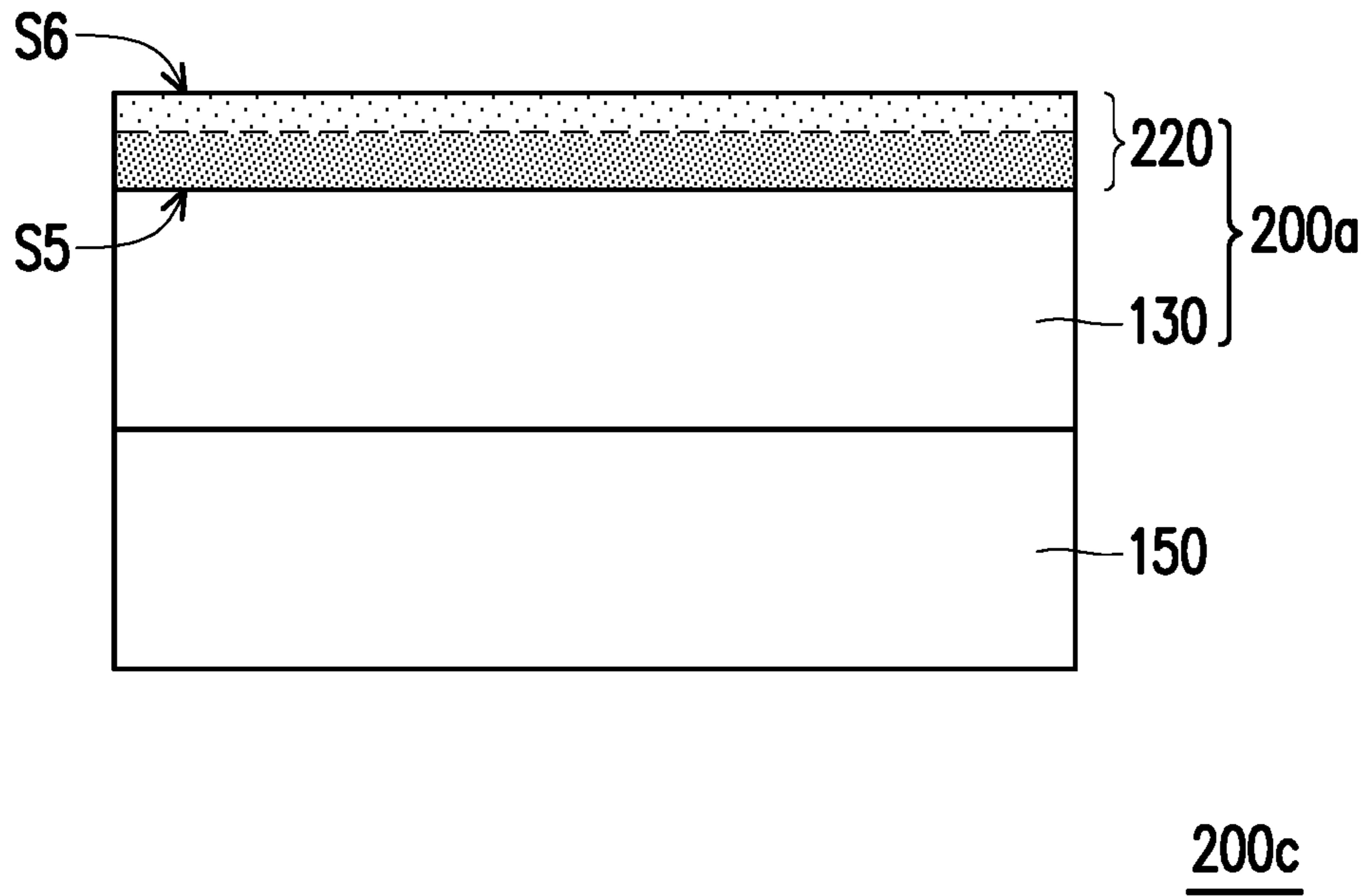


FIG. 2C

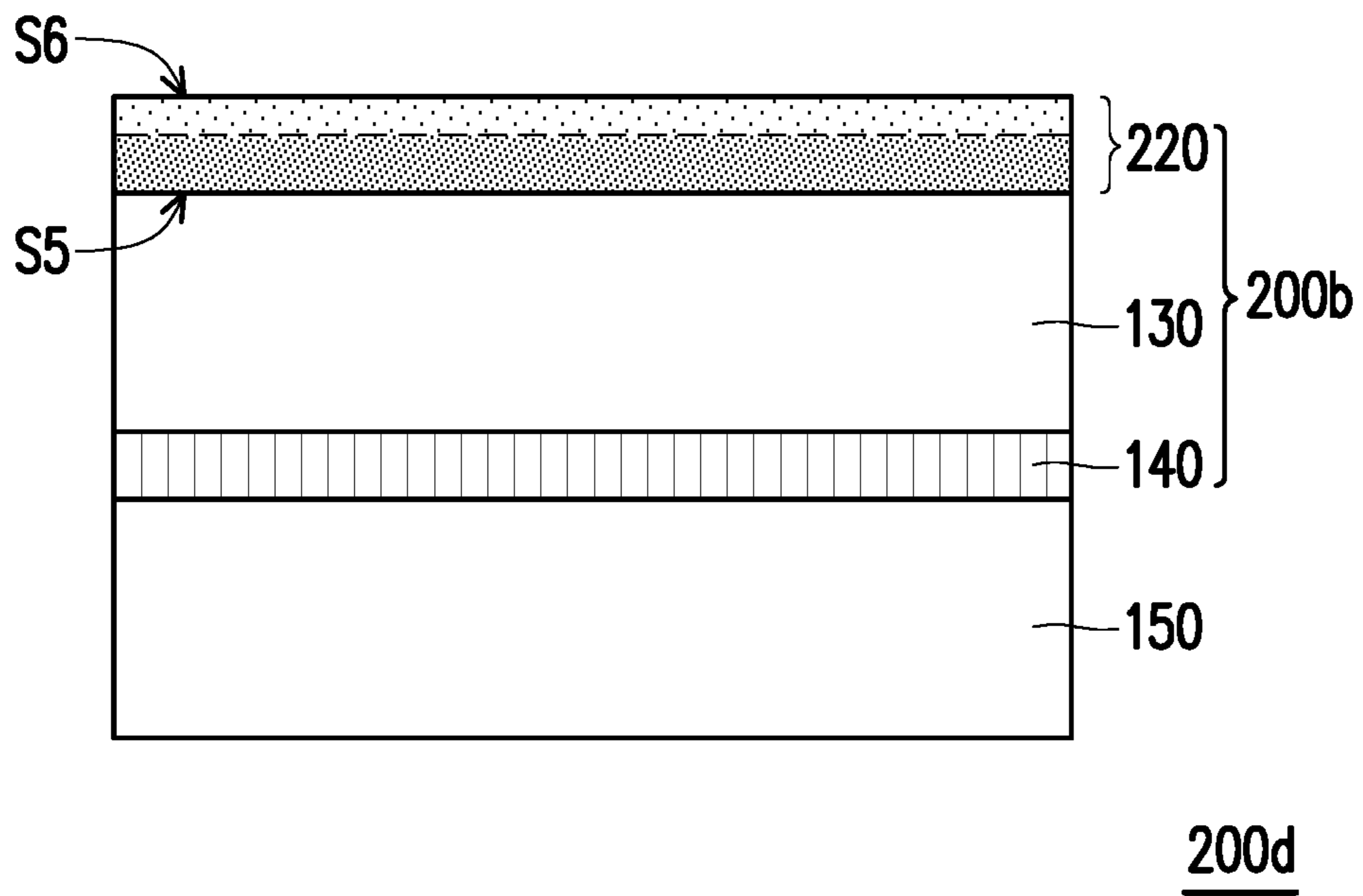
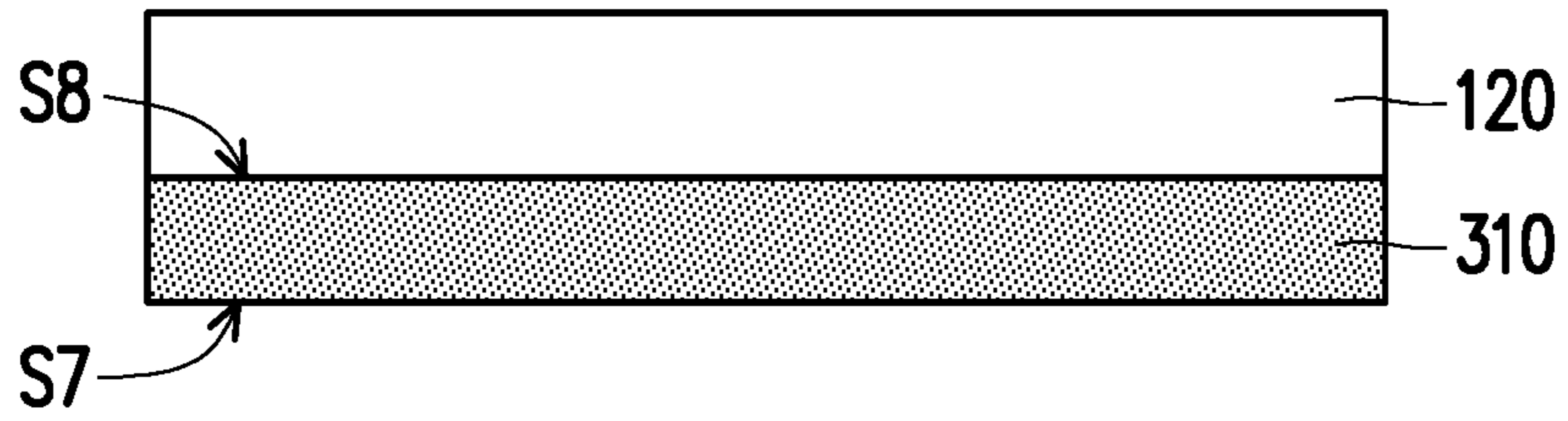
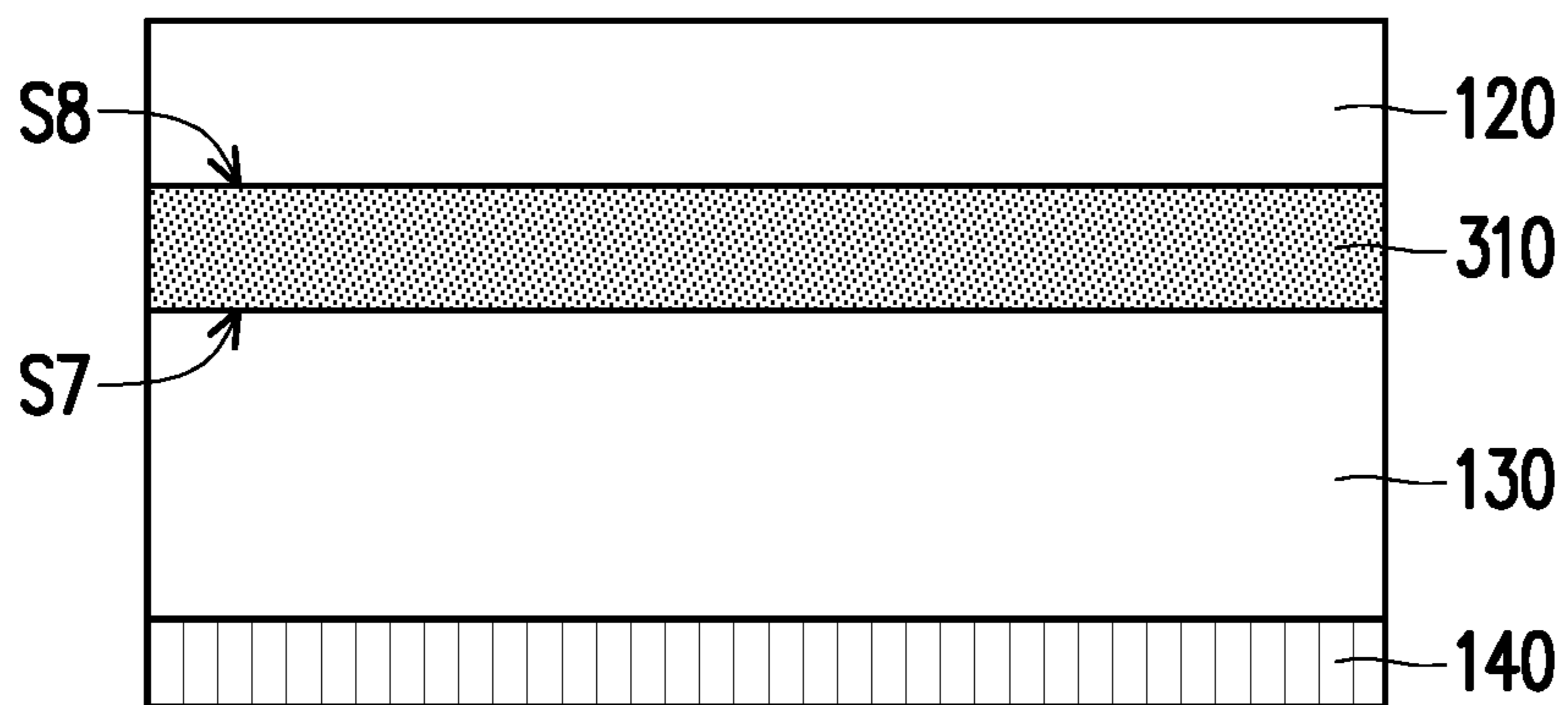


FIG. 2D



300a

FIG. 3A



300b

FIG. 3B

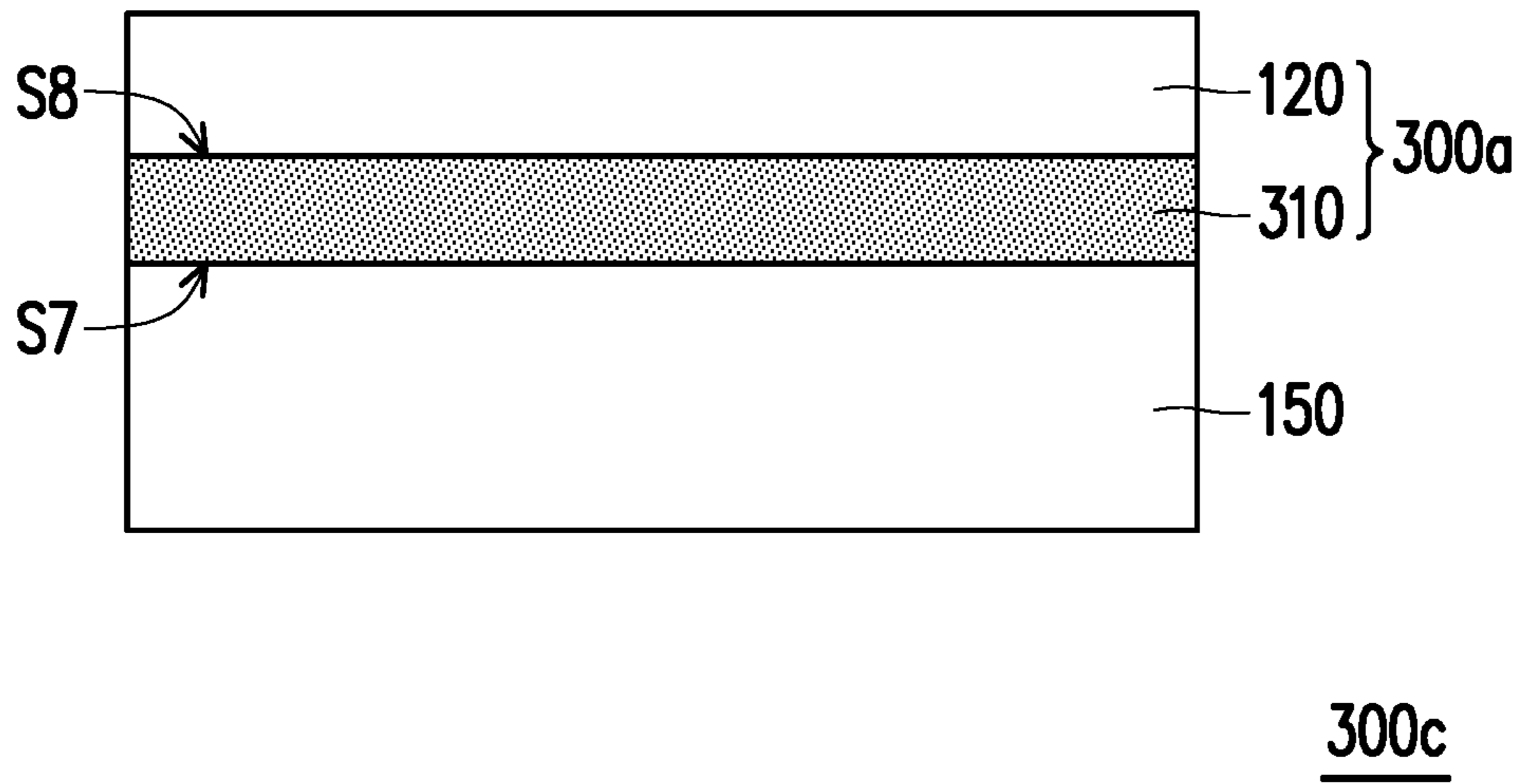


FIG. 3C

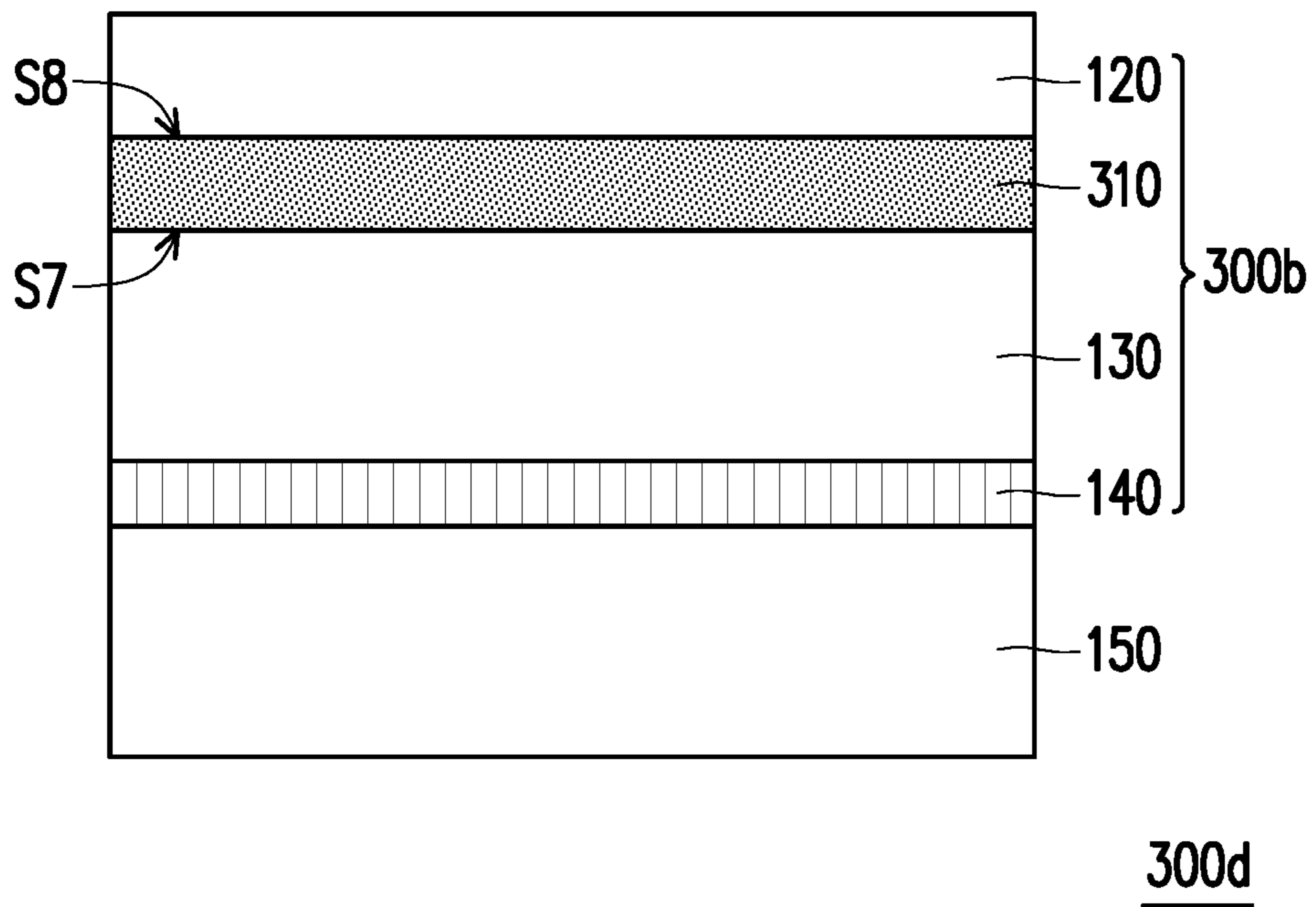


FIG. 3D

1**PROTECTIVE STRUCTURE AND
ELECTRONIC DEVICE WITH THE SAME****CROSS-REFERENCE TO RELATED
APPLICATION**

This application claims the priority benefits of U.S. provisional application Ser. No. 62/717,001, filed on Aug. 10, 2018, and Taiwan application serial no. 107147449, filed on Dec. 27, 2018. The entirety of the above-mentioned patent applications are hereby incorporated by reference herein.

TECHNICAL FIELD

The disclosure is related to a protective structure and an electronic device with the same.

BACKGROUND

As technology advances, electronic elements (such as soft electronic elements) often are provided with a hard coating layer (HC) on the surface to improve the scratch resistance thereof. However, when the thickness of the hard coating layer is increased, although the scratch resistance of the electronic element may be improved, the flexibility of the element is lowered. In addition, a surface or edge material cracking phenomenon occurs to the current hard coating layer structure after repeated folding, and phenomenon such as delamination of the bottom substrate may even occur, especially when the element is folded outward, since the hard coating layer needs to withstand greater stress, and the material cracking phenomenon more readily occurs after repeated outward folding. Therefore, how to overcome the above technical issues has become one of the issues that urgently need to be solved at present.

SUMMARY

A protective structure of an embodiment of the disclosure includes an auxiliary layer and a hard coating layer. The auxiliary layer has a first surface and a second surface opposite to the first surface. The hard coating layer is located on the second surface of the auxiliary layer. The Young's modulus of the auxiliary layer is gradually increased from the second surface toward the first surface.

A protective structure of an embodiment of the disclosure includes a substrate and a hard coating layer. The hard coating layer is located on the substrate. The hard coating layer has a first surface adjacent to the substrate and a second surface opposite to the first surface. The Young's modulus of the hard coating layer is gradually increased from the second surface toward the first surface.

A protective structure of an embodiment of the disclosure includes an auxiliary layer and a hard coating layer. The auxiliary layer has a first surface and a second surface opposite to the first surface. The hard coating layer is located on the second surface of the auxiliary layer. The Young's modulus of the auxiliary layer is greater than the Young's modulus of the hard coating layer, and the material of the auxiliary layer includes the same material as the hard coating layer.

An electronic device of an embodiment of the disclosure includes any of the protective structures above and an electronic element.

Several exemplary embodiments accompanied with figures are described in detail below to further describe the disclosure in details.

2**BRIEF DESCRIPTION OF THE DRAWINGS**

The accompanying drawings are included to provide further understanding, and are incorporated in and constitute a part of this specification. The drawings illustrate exemplary embodiments and, together with the description, serve to explain the principles of the disclosure.

FIG. 1A, FIG. 1B, FIG. 2A, FIG. 2B, FIG. 3A, and FIG. 3B are cross sections of a protective structure according to some embodiments of the disclosure.

FIG. 1C, FIG. 1D, FIG. 2C, FIG. 2D, FIG. 3C, and FIG. 3D are cross sections of an electronic device according to some embodiments of the disclosure.

FIG. 1E shows the relationship between the thickness direction and the Young's modulus in the protective structure of FIG. 1A.

**DETAILED DESCRIPTION OF DISCLOSED
EMBODIMENTS**

The following disclosure of the specification provides various embodiments or examples to implement various features of the various embodiments of the disclosure. The disclosure of the present specification describes specific examples of each element and their configuration in order to simplify the description. Of course, these specific examples are not intended to limit the disclosure. In addition, different examples in the description of the disclosure may adopt repeated reference numerals and/or wording. These repeated reference numerals or wording are not intended to limit the relationship of the various embodiments and/or the exterior structures for the purpose of simplicity and clarity. Furthermore, the disclosure of the present specification describing the forming of a first feature on or above a second feature includes an embodiment in which the formed first feature is in direct contact with the second feature, and also includes an embodiment in which an additional feature may be formed between the first feature and the second feature, such that the first feature may not be in direct contact with the second feature. In addition, the concentration referred to in the present specification may represent a weight percent concentration (wt %) or a volume percent concentration (vol %) unless otherwise specified. The dimensions of the elements in the drawings are drawn for convenience of description and do not represent their actual element size ratios.

An embodiment of the disclosure provides a protective structure and an electronic device having improved scratch resistance and having good flexibility at the same time, and the material cracking phenomenon after the electronic device is folded (especially folded outward) may also be reduced, thereby increasing the service life and reliability of the electronic device.

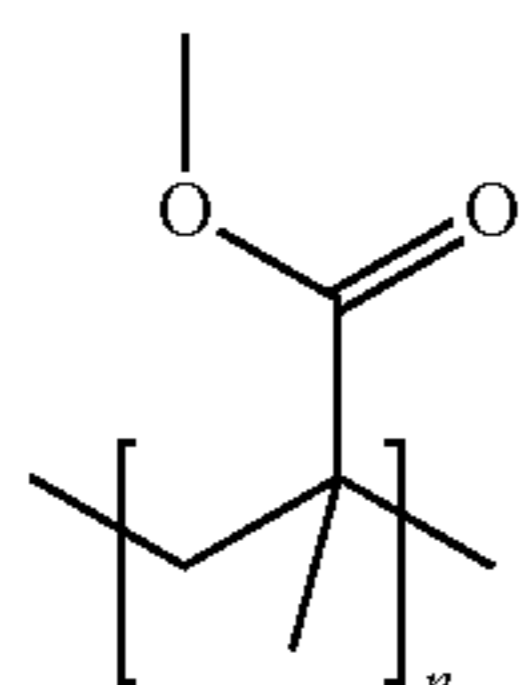
Referring to FIG. 1A, a protective structure **100a** includes an auxiliary layer **110** and a hard coating layer **120** located on the auxiliary layer **110**. The auxiliary layer **110** may be a scratch resistant auxiliary layer, and the hard coating layer **120** may be a protective anti-stress layer. The auxiliary layer **110** has a first surface **S1** and a second surface **S2** opposite to the first surface **S1**. The hard coating layer **120** has a top surface **S3** and a bottom surface **S4** opposite to the top surface **S3**. The hard coating layer **120** is located on the second surface **S2** of the auxiliary layer **110**. In some embodiments, the second surface **S2** of the auxiliary layer **110** is closer to the hard coating layer **120** than the first surface **S1** of the auxiliary layer **110**. In some embodiments, the bottom surface **S4** of the hard coating layer **120** is in direct contact with the second surface **S2** of the auxiliary

layer 110. In some embodiments, the auxiliary layer 110 and the hard coating layer 120 may be unpatterned layers. In other words, the hard coating layer 120 may completely cover the second surface S2 of the auxiliary layer 110.

The Young's modulus of the auxiliary layer 110 is different from the Young's modulus of the hard coating layer 120. In some embodiments, the Young's modulus of the hard coating layer 120 is less than or equal to the Young's modulus of the auxiliary layer 110. In some embodiments, the Young's modulus of the hard coating layer 120 is a constant, and the Young's modulus of the auxiliary layer 110 is a gradient. The Young's modulus of the hard coating layer 120 is almost kept a constant from the top surface S3 to the bottom surface S4 and is less than or equal to the Young's modulus of the auxiliary layer 110. The Young's modulus of the auxiliary layer 110 is gradually increased from the second surface S2 toward the first surface S1.

In some embodiments, the Young's modulus of the hard coating layer 120 may be 1 to 60 GPa (10^9 Pa). In some embodiments, the Young's modulus of the hard coating layer 120 may be 1 to 40 GPa. In some embodiments, the Young's modulus of the hard coating layer 120 may be 1 to 30 GPa. In some embodiments, the Young's modulus of the auxiliary layer 110 may be 5 to 100 GPa. In some embodiments, the Young's modulus of the auxiliary layer 110 may be 5 to 60 GPa. In some embodiments, the Young's modulus of the auxiliary layer 110 may be 5 to 40 GPa. In some embodiments, the ratio of the Young's modulus of the hard coating layer 120 to the Young's modulus of the auxiliary layer 110 may range from 0.01 to 1. In some embodiments, the ratio of the Young's modulus of the hard coating layer 120 to the Young's modulus of the auxiliary layer 110 may range from 0.016 to 1. In some embodiments, the ratio of the Young's modulus of the hard coating layer 120 to the Young's modulus of the auxiliary layer 110 may range from 0.025 to 1.

The auxiliary layer 110 may include an organic material, and the organic material may be doped with an inorganic material. In some embodiments, the organic material may be a photocurable material, but the disclosure is not limited thereto. In some embodiments, the organic material may be a monomer material, a polymer material, or a combination of the foregoing. The organic material may be a monomer material having a molecular weight of 60 g/mol to 500 g/mol or a polymer material having a weight-average molecular weight (Mw) of 500 g/mol to 200,000 g/mol. The organic material may include pentaerythritol trimethacrylate, acrylate material, or a combination of the foregoing. In some embodiments, the acrylic structural formula may be represented by the following Formula (1)



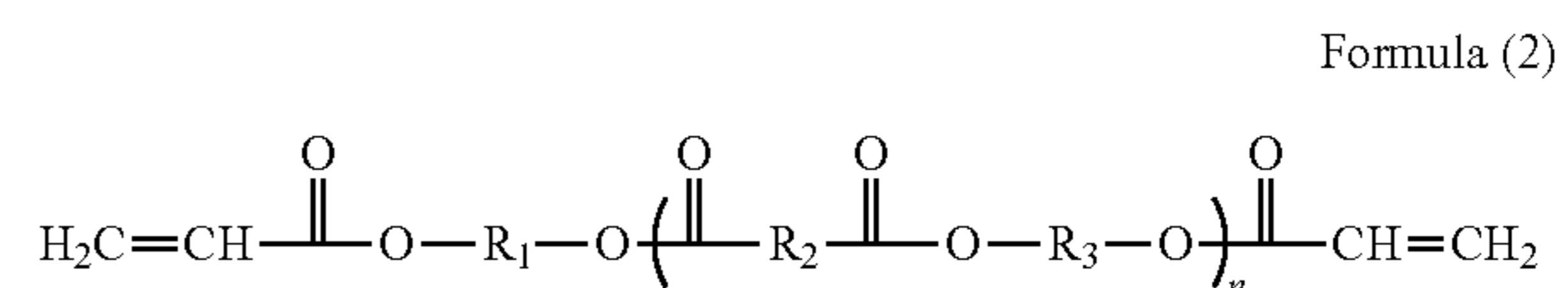
Formula (1)

wherein n is, for example, 1 to 2000.

The inorganic material of the auxiliary layer 110 may be a high hardness material. That is, the hardness of the inorganic material may be higher than the hardness of the organic material so as to increase the Young's modulus of the auxiliary layer 110 by doping the inorganic material. In other words, the doping concentration of the inorganic material of the auxiliary layer 110 is positively correlated with the Young's modulus thereof, and the Young's modulus of the auxiliary layer 110 may be changed by adjusting the doping concentration of the inorganic material, so that the Young's modulus of the auxiliary layer 110 is gradually increased from the second surface S2 toward the first surface S1. In some embodiments, the concentration of the inorganic material is gradually increased from 5 wt % to 45 wt % (weight percent concentration), and the Young's modulus of the auxiliary layer 110 at the second surface S2 is gradually increased from 5 GPa such that the Young's modulus of the auxiliary layer 110 at the first surface S1 is increased to 7 to 10 GPa, but the disclosure is not limited thereto.

The inorganic material is, for example, a ceramic material. The ceramic material is, for example, an oxide. The oxide may include modified or unmodified silicon dioxide, titanium oxide, zirconium oxide, or a combination thereof. The inorganic material is, for example, a nanoparticle. In some embodiments, the particle size of the inorganic material may be less than 50 nm. In some other embodiments, the particle size of the inorganic material may be between 20 nm and 30 nm. In still other embodiments, the particle size of the inorganic material may be between 10 nm and 30 nm. Further, in some embodiments, the average particle size of the inorganic material may be less than 50 nm. In some other embodiments, the average particle size of the inorganic material may be between 20 nm and 30 nm. In still other embodiments, when the average particle size of the inorganic material is less than 25 nm, the transmittance of the subsequently completed electronic device may be improved, but the disclosure is not limited thereto.

In an embodiment, the organic material is, for example, an acrylic material, and the inorganic material is, for example, silicon dioxide. The structural formula of the acrylic material may be represented by the following Formula (2) or Formula (3).



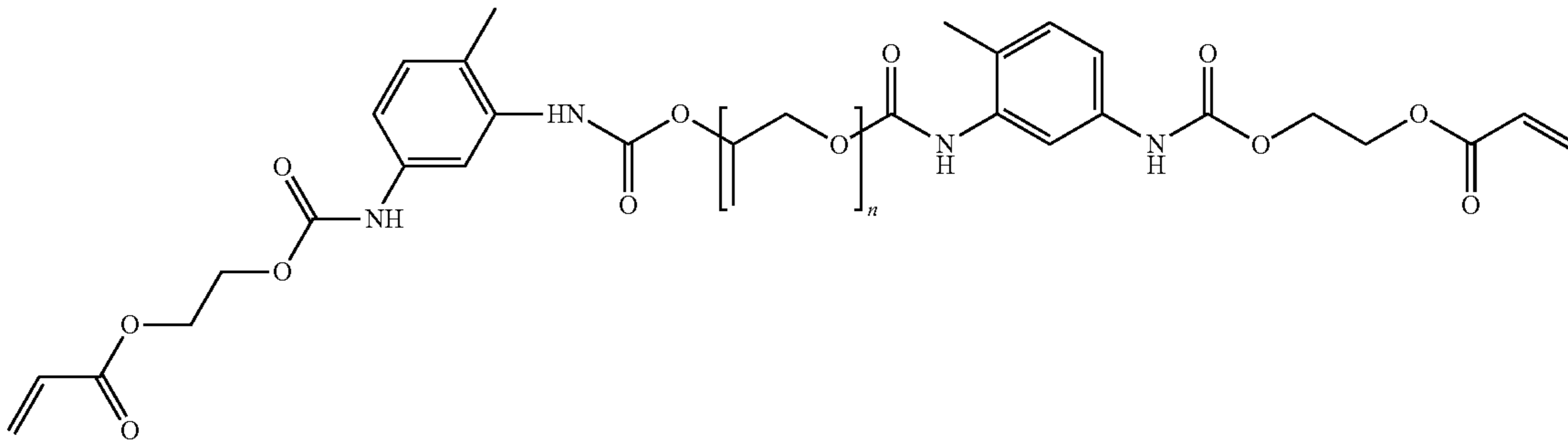
Formula (2)

wherein R_1 and R_3 are branched or straight alkyl chains (for example, C1 to 20 alkyl groups), R_2 is an alkylene group (for example, $-(\text{CH}_2)_x-$, and x is an integer between 1 and 20), and n is greater than or equal to 1.

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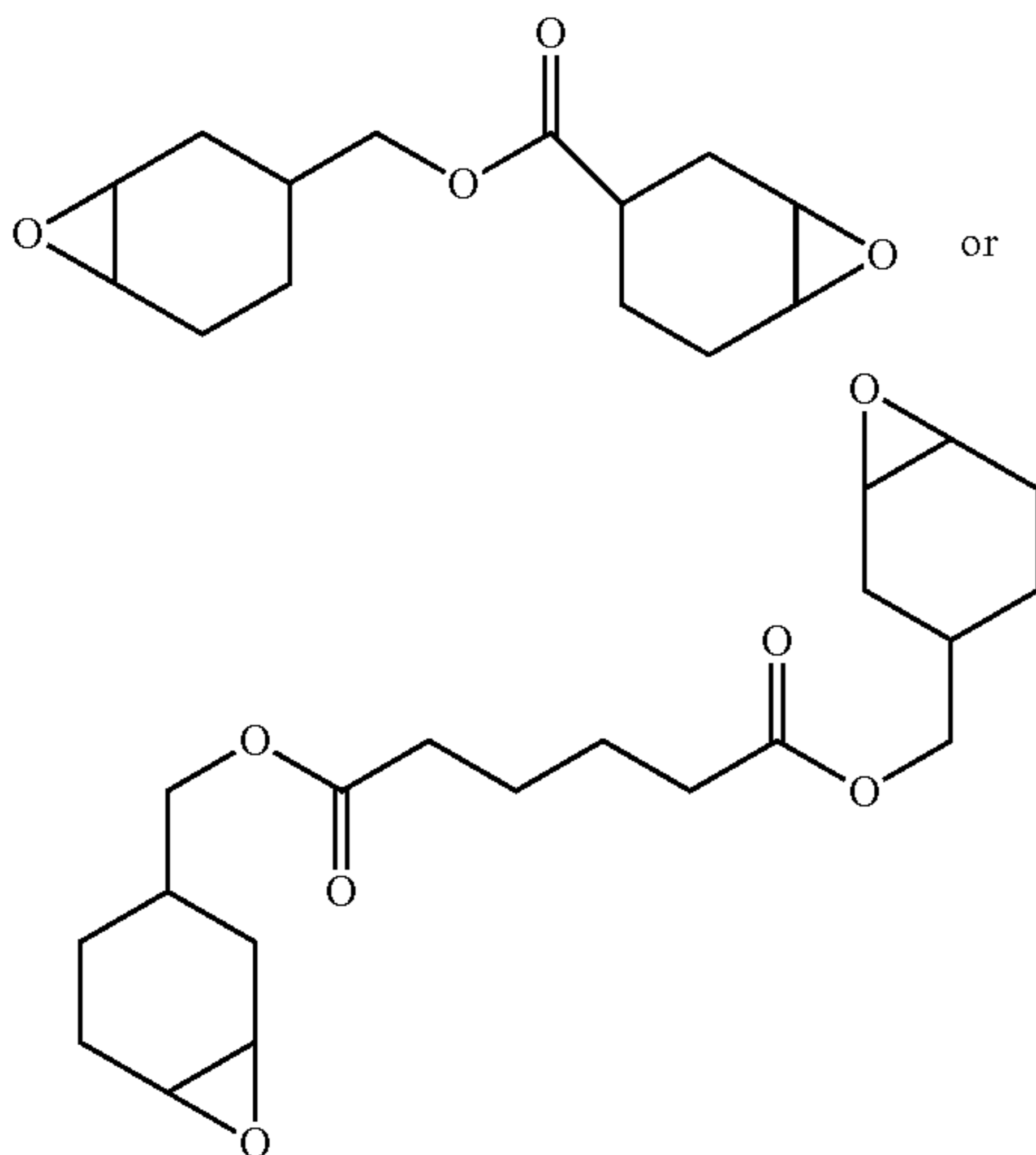
Formula (3)



wherein n is 0 or greater than or equal to 1.

In another embodiment, the organic material is, for example, an epoxy resin, and the inorganic material is, for example, silicon dioxide. The structural formula of the epoxy resin may be represented by Formula (4) below.

Formula (4)



In some embodiments, the method of doping the inorganic material in the organic material may include first uniformly dispersing the inorganic material in the organic material using a solvent. For example, a solvent (such as an ester solvent such as EA) may be used to uniformly disperse a polar inorganic material in a non-polar organic material. Next, a soft bake and a curing process are performed to volatilize the solvent in the organic material. In some embodiments, the soft bake temperature is, for example, 85° C. to 105° C. The photocuring process may be performed, for example, using ultraviolet light (UV). In some embodiments, the photocuring energy is, for example, 500 mj (mini joule) to 4500 mj. In some embodiments, the photocuring energy is, for example, 500 mj to 2500 mj.

Since the volatilization of the solvent causes the polar inorganic material to not be effectively and uniformly dispersed in the non-polar organic material, the inorganic material in the organic material is deposited by gravity to the first surface S1 of the auxiliary layer 110, and therefore the doping concentration of the inorganic material is higher toward the first surface S1 of the auxiliary layer 110. In some

embodiments, the inorganic material may be surface modified prior to doping such that the inorganic material is more uniformly dispersed in the organic material prior to the step of photocuring, thereby enhancing the effect of subsequent deposition. In other embodiments, the inorganic material in the auxiliary layer 110 may achieve the doping effect thereof more effectively via a method of controlling the process parameters such as adjusting the soft bake temperature, the photocuring energy, and the like.

The hard coating layer 120 may include an organic material. In an embodiment, the hard coating layer 120 may be an organic material that is not doped with an inorganic material. In another embodiment, the hard coating layer 120 may also be an organic material lightly doped with an inorganic material, and the concentration of the inorganic material may be between 3 wt % and 25 wt %. The organic material and the inorganic material of the hard coating layer 120 may be the same as or similar to the organic material and the inorganic material of the above auxiliary layer 110, and are not repeated herein.

In an embodiment in which the hard coating layer 120 is an organic material not doped with an inorganic material, the organic material of the auxiliary layer 110 may be the same as the organic material of the hard coating layer 120 to enhance the adhesion of the interface between the auxiliary layer 110 and the hard coating layer 120 so as to reduce the possibility of separation between the auxiliary layer 110 and the hard coating layer 120. For example, the organic material of the auxiliary layer 110 and the organic material of the hard coating layer 120 may be acrylic materials.

In an embodiment in which the hard coating layer 120 is an organic material lightly doped with an inorganic material, the organic material of the auxiliary layer 110 may be the same as the organic material of the hard coating layer 120. In other words, the auxiliary layer 110 and the hard coating layer 120 use the same organic material as the host material to improve the adhesion of the interface between the auxiliary layer 110 and the hard coating layer 120 to reduce the possibility of separation between the auxiliary layer 110 and the hard coating layer 120. In some embodiments, the inorganic material doped in the hard coating layer 120 may be the same as the inorganic material doped in the auxiliary layer 110, and the concentration of the inorganic material doped in the hard coating layer 120 is less than or equal to the concentration of the inorganic material doped in the auxiliary layer 110. In some embodiments, the inorganic material doped in the hard coating layer 120 may be different from the inorganic material doped in the auxiliary layer 110, and the concentrations of the inorganic materials of the hard coating layer 120 and the concentrations of the inorganic

materials of the auxiliary layer **110** may be determined according to actual design, and any concentration is within the scope of the disclosure provided the Young's modulus of the auxiliary layer **110** is gradually increased from the second surface **S2** toward the first surface **S1**.

Referring further to FIG. 1A, in some embodiments, the auxiliary layer **110** has a first portion **P1** and a second portion **P2** located on the first portion **P1**. The first portion **P1** is a portion of the auxiliary layer **110** away from the hard coating layer **120**, the second portion **P2** is a portion of the auxiliary layer **110** adjacent to the hard coating layer **120**, and the first portion **P1** is farther away from the hard coating layer **120** than the second portion **P2**. The lower surface of the first portion **P1** is the first surface **S1** of the auxiliary layer **110**, the upper surface of the second portion **P2** is the second surface **S2** of the auxiliary layer **110**, and the second portion **P2** is located between the first portion **P1** and the hard coating layer **120**.

The ratio of a thickness **T1** of the first portion **P1** of the auxiliary layer **110** to a total thickness T_A of the auxiliary layer **110** is greater than the ratio of a thickness **T2** of the second portion **P2** of the auxiliary layer **110** to the total thickness T_A of the auxiliary layer **110**. The thickness **T1** of the first portion **P1** is, for example, $\frac{4}{5}$ to $\frac{9}{10}$ of the total thickness T_A of the auxiliary layer **110**, and the thickness **T2** of the second portion **P2** is, for example, $\frac{1}{5}$ to $\frac{1}{10}$ of the thickness T_A of the auxiliary layer **110**. In some embodiments, the Young's modulus of the first portion **P1** may be a gradient, the Young's modulus of the second portion **P2** may be kept a constant or be a gradient, and the Young's modulus of the hard coating layer **120** may be kept a constant or be a gradient. In some embodiments, the Young's modulus of the first portion **P1** is greater than the Young's modulus of the hard coating layer **120**, the Young's modulus of the second portion **P2** is greater than or equal to the Young's modulus of the hard coating layer **120**, and the Young's modulus of the first portion **P1** is greater than the Young's modulus of the second portion **P2**. The minimum value of the Young's modulus in the first portion **P1** is greater than the maximum value of the Young's modulus of the hard coating layer **120**, the minimum value of the Young's modulus of the second portion **P2** is greater than or equal to the maximum value of the Young's modulus of the hard coating layer **120**, and the minimum value of the Young's modulus of the first portion **P1** is greater than the maximum value of the Young's modulus of the second portion **P2**. In some embodiments, the Young's modulus of the first portion **P1** is 5 to 50 GPa, and the Young's modulus of the second portion **P2** is 3 to 20 GPa, but the disclosure is not limited thereto. In some embodiments, the Young's modulus of the first portion **P1** is 7 to 45 GPa, and the Young's modulus of the second portion **P2** is 4 to 20 GPa, but the disclosure is not limited thereto.

The weight percent concentration of the inorganic material of the first portion **P1** is greater than the weight percent concentration of the inorganic material of the second portion **P2**. In some embodiments, the concentration of the inorganic material of the first portion **P1** is 10 wt % to 60 wt %, or 5 vol % to 30 vol %. The concentration of the inorganic material of the second portion **P2** is 0 wt % to 20 wt %, or 0 vol % to 10 vol %. In other words, the first portion **P1** is doped with an inorganic material, and the second portion **P2** may not be doped with an inorganic material, or is lightly doped with an inorganic material.

It should be noted that the disclosure does not limit the method in which the Young's modulus of the auxiliary layer **110** is gradually increased from the second surface **S2**

toward the first surface **S1**, such as doping with an inorganic material, and any method is within the scope of the disclosure as long as the Young's modulus of the auxiliary layer **110** is gradually increased from the second surface **S2** toward the first surface **S1**.

FIG. 1B is a cross section of a protective structure according to another embodiment of the disclosure.

Referring to FIG. 1B, a protective structure **100b** is similar to the protective structure **100a** of FIG. 1A, and the difference is that the protective structure **100b** further includes a substrate **130** and an optical structure layer **140**. In the embodiment, one side of the substrate **130** is the auxiliary layer **110**, and another side of the substrate **130** is the optical structure layer **140**.

The substrate **130** may be a single material substrate, such as an organic material or inorganic material. The organic material may include, for example, polyimine (PI), polymethyl methacrylate (PMMA), polycarbonate (PC), polyethersulfone (PES), polyamine (PA), polyethylene terephthalate (PET), polyether ether ketone (PEEK), polyethylene naphthalate (PEN), polyethyleneimine (PEI), polyurethane (PU), polydimethyl siloxane (PDMS), acrylic, polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA), ether-containing polymer, polyolefin, or a combination of the above, but is not limit thereto. The material of the inorganic material includes single metal, metal oxide, non-metal oxide, non-metal nitride, ceramic, or the like, or a composite material composed of the above materials, but is not limited thereto. The inorganic material is, for example, diamond-like carbon (DLC), silicon nitride, silicon oxide, silicon oxynitride, aluminum oxide, aluminum titanium dioxide, titanium oxide, titanium oxynitride, or a solution gas barrier (SGB) (SGB is, for example, polysilazane), and the like. In some embodiments, the substrate **130** may be a composite substrate including an organic material and an inorganic material. The composite substrate of the organic material and the inorganic material refers to a substrate formed by mixing an organic material and an inorganic material.

In some embodiments, the optical structure layer **140** may be a circular polarizer (CPL) or a light filter structure. The CPL is, for example, a polarizing layer and a phase retardation layer, wherein the polarizing layer may be a linear polarizing layer, and the phase retardation layer may be a $\frac{1}{4}$ wavelength retardation layer. The light filter structure is, for example, a black filter layer, a color filter layer, or a combination of both.

The Young's modulus of the substrate **130** is different from the Young's modulus of the hard coating layer **120**. In some embodiments, the Young's modulus of the substrate **130** is less than the Young's modulus of the auxiliary layer **110** and less than the Young's modulus of the hard coating layer **120**. The Young's modulus of the substrate **130** is, for example, 3 to 10 GPa. In other words, the order of the Young's modulus of each layer of the protective structure **100b** is, from low to high, the substrate **130**, the hard coating layer **120**, and the auxiliary layer **110**. The Young's modulus of the optical structure layer **140** may be 1 to 20 GPa, and the thickness thereof may be 1 to 50 μm (micrometer).

In some embodiments, the manufacturing method of the protective structure **100b** may include first coating a solution including a solvent and an organic material doped with an inorganic material on a surface of the substrate **130**, followed by a soft bake process. Next, a photocuring process is performed to form the auxiliary layer **110**. Thereafter, a solution including an organic material is coated on the auxiliary layer **110**, and then a photocuring process is

performed to form the hard coating layer **120**. The optical structure layer **140** may be attached to another surface of the substrate **130** via an adhesive layer (not shown), or directly formed on the substrate **130** via wet coating or dry film forming.

In other embodiments, the protective structure is similar to the protective structure **100b** described above, but does not include the optical structure layer **140**.

FIG. **1C** is a cross section of an electronic device having a protective structure according to some embodiments of the disclosure.

Referring to FIG. **1C**, an electronic device **100c** includes a protective structure **100a** as shown in FIG. **1A** and an electronic element **150**. The protective structure **100a** is disposed on the electronic element **150**. In some embodiments, the electronic element **150** is in contact with the first surface **S1** of the auxiliary layer **110**. In another embodiment, the protective structure **100a** may be bonded to the electronic element **150** via an adhesive layer (not shown) to form the electronic device **100c**, but is not limited thereto.

The material of the adhesive layer is, for example, a resin film, an optical transparent adhesive (OCA), a hot melt adhesive, an optical pressure sensitive adhesive (PSA), or an optical pressure sensitive resin (OCR), but the disclosure is not limited thereto. In some embodiments, the electronic element **150** may be a wire, an electrode, a resistor, an inductor, a capacitor, a transistor, a diode, a switching element, an amplifier, a processor, a controller, a thin film transistor, a touch element, a pressure sensing element, a microelectromechanical element, a feedback element, a display, a touch display element, a single chip module, a multi-chip module, an OLED (organic light-emitting diode) lighting, or other suitable electronic elements. In other embodiments, the electronic element **150** may also be an optical element or an element having a light filter, but the disclosure is not limited thereto. In an embodiment, the display may be an active matrix display or a passive matrix display, and the active matrix display may be an organic light-emitting diode (OLED) display, a micro LED (micro light-emitting diode) or other suitable displays.

In some embodiments, the Young's modulus of the electronic element **150** may be 15 to 100 GPa, the Young's modulus of the auxiliary layer **110** may be 5 to 100 GPa, and the Young's modulus of the hard coating layer **120** may be 1 to 60 GPa. In still other embodiments, the Young's modulus of the electronic element **150** may be 15 to 100 GPa, the Young's modulus of the auxiliary layer **110** may be 5 to 60 GPa, and the Young's modulus of the hard coating layer **120** may be 1 to 40 GPa. In some other embodiments, the Young's modulus of the electronic element **150** may be 15 to 100 GPa, the Young's modulus of the auxiliary layer **110** may be 5 to 40 GPa, and the Young's modulus of the hard coating layer **120** may be 1 to 30 GPa.

In some embodiments, the ratio of the Young's modulus of the hard coating layer **120** to the Young's modulus of the auxiliary layer **110** may range from 0.01 to 1, and the ratio of the Young's modulus of the auxiliary layer **110** to the Young's modulus of the electronic element **150** may range from 0.1 to 6.7. In other embodiments, the ratio of the Young's modulus of the hard coating layer **120** to the Young's modulus of the auxiliary layer **110** may range from 0.016 to 1, and the ratio of the Young's modulus of the auxiliary layer **110** to the Young's modulus of the electronic element **150** may range from 0.1 to 4. In still other embodiments, the ratio of the Young's modulus of the hard coating layer **120** to the Young's modulus of the auxiliary layer **110** may range from 0.025 to 1, and the ratio of the Young's

modulus of the auxiliary layer **110** to the Young's modulus of the electronic element **150** may range from 0.1 to 2.7.

Referring further to FIG. **1C**, in some embodiments, a thickness T_E of the electronic element **150** in the protective structure **100c** may be 30 to 200 μm , the thickness T_A of the auxiliary layer **110** may be 10 to 40 μm , and a thickness T_C of the hard coating layer **120** may be 1 to 30 μm . In some embodiments, the ratio of the thickness T_C of the hard coating layer **120** to the thickness T_A of the auxiliary layer **110** (i.e., T_C/T_A) may range from 0.025 to 3, and the ratio of the thickness T_A of the auxiliary layer **110** to the thickness T_E of the electronic element **150** (i.e., T_A/T_E) may range from 0.05 to 1.4.

FIG. **1D** is a cross section of an electronic device having a protective structure according to some other embodiments of the disclosure.

Referring to FIG. **1D**, an electronic device **100d** includes the protective structure **100b** as shown in FIG. **1B** and the electronic element **150**. The protective structure **100b** is disposed on the electronic element **150**. In some embodiments, the surface of the electronic element **150** may be in contact with the surface of the optical structure layer **140** away from the substrate **130**. In other words, the optical structure layer **140** is disposed between the electronic element **150** and the substrate **130**. The characteristics of the remaining layers other than the electronic element **150** in the electronic device **100d** are the same as or similar to the protective structure **100b** of FIG. **1B**. The Young's modulus of the electronic element **150** may be 15 to 100 GPa.

Since the Young's modulus of the auxiliary layer **110** of the protective structures **100a** to **100b** of FIG. **1A** and FIG. **1B** is gradually increased from the second surface **S2** toward the first surface **S1**, the electronic device **100c** having the protective structure **100a** (FIG. **1C**) and the electronic device **100d** having the protective structure **100b** (FIG. **1D**) may have improved scratch resistance and have good flexibility at the same time. Therefore, the material cracking phenomenon of the electronic devices **100c** to **100d** after folding (especially outward folding) may be reduced, thereby increasing the service life and reliability of the electronic devices **100c** to **100d**.

It is to be noted that the following embodiments adopt the same reference numerals and some of the content of the above embodiments, wherein the same reference numerals are used to refer to the same or similar elements, and descriptions of the same technical content are omitted. The description of the omitted portions is provided in the foregoing embodiments and is not repeated in the following embodiments.

Referring to FIG. **2A**, a protective structure **200a** includes the substrate **130** and a hard coating layer **220** located on the substrate **130**. The hard coating layer **220** has a first surface **S5** adjacent to the substrate **130** and a second surface **S6** opposite to the first surface **S5**. The substrate **130** is located on the first surface **S5** of the hard coating layer **220**. The Young's modulus of the hard coating layer **220** is different from the Young's modulus of the substrate **130**. In some embodiments, the Young's modulus of the hard coating layer **220** is greater than the Young's modulus of the substrate **130**. In some embodiments, the Young's modulus of the substrate **130** is a constant, and the Young's modulus of the hard coating layer **220** is a gradient. The Young's modulus of the substrate **130** is kept a constant from the top to the bottom and is less than the Young's modulus of the hard coating layer **220**. The Young's modulus of the hard coating layer **220** is gradually increased from the second surface **S6**

toward the first surface **S5**. The Young's modulus of the hard coating layer **220** ranges, for example, from 1 GPa to 100 GPa.

In some embodiments, the hard coating layer **220** may include an organic material and an inorganic material may be doped in the organic material. The doping concentration of the inorganic material is positively correlated with the Young's modulus of the hard coating layer **220**, so the Young's modulus of the hard coating layer **220** may be changed by adjusting the doping concentration of the inorganic material. Gradually increasing the concentration of the inorganic material from 2 wt % to 50 wt % may cause the Young's modulus of the hard coating layer **220** to be gradually increased from the second surface **S6** toward the first surface **S5**, but the disclosure is not limited thereto. The inorganic material and organic material of the hard coating layer **220** may be similar to those described for the inorganic material and the organic material of the auxiliary layer **110** of FIG. 1A, and details are not repeated herein.

In some embodiments, the manufacturing method of the protective structure **200a** may include first coating a solution including a solvent and an organic material doped with an inorganic material on the substrate **130**, followed by a soft bake process. Next, a photocuring process is performed to form the hard coating layer **220**.

Referring further to FIG. 2A, the hard coating layer **220** has a first portion **P3** and a second portion **P4** located on the first portion **P3**. The first portion **P3** is a portion of the hard coating layer **220** adjacent to the substrate **130**, and the second portion **P4** is a portion of the hard coating layer **220** away from the substrate **130**. That is, the first portion **P3** is located between the second portion **P4** and the substrate **130**. In other words, the lower surface of the first portion **P3** is the first surface **S5** of the hard coating layer **220**, and the upper surface of the second portion **P4** is the second surface **S6** of the hard coating layer **220**.

In some embodiments, the Young's modulus of the first portion **P3** and the Young's modulus of the second portion **P4** are both greater than the Young's modulus of the substrate **130**, and the Young's modulus of the first portion **P3** is greater than the Young's modulus of the second portion **P4**. In some embodiments, the Young's modulus of the first portion **P3** is 5 to 50 GPa, and the Young's modulus of the second portion **P4** is 3 to 20 GPa, but the disclosure is not limited thereto.

In the hard coating layer **220**, the average doping concentration of the inorganic material of the first portion **P3** is greater than the average doping concentration of the inorganic material of the second portion **P4**. In some embodiments, the concentration of the inorganic material of the first portion **P3** is 10 wt % to 60 wt %, or 5 vol % to 30 vol %. The concentration of the inorganic material of the second portion **P4** is 0 wt % to 20 wt %, or 0 vol % to 10 vol %. In some embodiments, the concentration of the inorganic material doped in the first portion **P3** is 10 wt % to 60 wt %, or 5 vol % to 30 vol %. The concentration of the inorganic material doped in the second portion **P4** is 2 wt % to 20 wt %, or 1 vol % to 10 vol %.

The method of doping the inorganic material of the disclosure is not particularly limited as long as the Young's modulus of the hard coating layer **220** is gradually increased from the second surface **S6** toward the first surface **S5**, and any method satisfying the condition is within the scope of the disclosure.

Further, in some embodiments, a thickness **T3** of the first portion **P3** is greater than a thickness **T4** of the second portion **P4**. In some embodiments, the thickness **T3** of the

first portion **P3** may be $\frac{4}{5}$ to $\frac{9}{10}$ of the thickness **T5** of the hard coating layer **220**, and the thickness **T4** of the second portion **P4** may be $\frac{1}{5}$ to $\frac{1}{10}$ of the thickness **T5** of the hard coating layer **220**.

Referring to FIG. 2B, a protective structure **200b** is similar to the protective structure **200a** of FIG. 2A, and the difference is that the protective structure **200b** further includes the optical structure layer **140**. In the embodiment, one side of the substrate **130** is the hard coating layer **220**, and another side of the substrate **130** is the optical structure layer **140**. In some other embodiments, the protective structure is similar to the protective structure **200b**, but does not include the optical structure layer **140**.

Referring to FIG. 2C, an electronic device **200c** includes the protective structure **200a** as shown in FIG. 2A and the electronic element **150**. The protective structure **200a** is disposed on the electronic element **150**. In other words, the substrate **130** is sandwiched between the hard coating layer **220** and the electronic element **150**.

Referring to FIG. 2D, an electronic device **200d** includes the protective structure **200b** as shown in FIG. 2B and the electronic element **150**. The protective structure **200b** is disposed on the electronic element **150**, that is, the optical structure layer **140** is sandwiched between the substrate **130** and the electronic element **150**.

The Young's modulus of the hard coating layer **220** of the protective structures **200a** to **200b** is gradually increased from the second surface **S6** toward the first surface **S5**, so the electronic device **200c** having the protective structure **200a** and the electronic device **200d** having the protective structure **200b** may have improved scratch resistance and have good flexibility at the same time, and the material cracking phenomenon of the electronic devices **200c** to **200d** after folding (especially outward folding) may also be reduced, so the service life and reliability of the electronic devices **200c** to **200d** may be increased. In addition, since the protective structures **200a** to **200b** adopt only a single layer of the hard coating layer **220**, process steps may be further reduced to improve production efficiency.

Referring to FIG. 3A, a protective structure **300a** includes an auxiliary layer **310** and the hard coating layer **120** located on the auxiliary layer **310**. The auxiliary layer **310** has a first surface **S7** and a second surface **S8** opposite to the first surface **S7**, and the hard coating layer **120** is located on the second surface **S8** of the auxiliary layer **310**. In some embodiments, the second surface **S8** of the auxiliary layer **310** is closer to the hard coating layer **120** than the first surface **S7** of the auxiliary layer **310**. The Young's modulus of the auxiliary layer **310** is different from the Young's modulus of the hard coating layer **120**. The Young's modulus of the auxiliary layer **310** is greater than the Young's modulus of the hard coating layer **120**. In some embodiments, the auxiliary layer **310** and the hard coating layer **120** respectively have a fixed Young's modulus. The material of the auxiliary layer **310** is a homogenous structure to the hard coating layer **120**. The material of the auxiliary layer **310** may be the same as that of the hard coating layer **120** to improve the adhesion at the interface between the auxiliary layer **310** and the hard coating layer **120** and to reduce the possibility of separation between the auxiliary layer **310** and the hard coating layer **120**.

In some embodiments, the auxiliary layer **310** may be an organic material, and an inorganic material may be doped in the organic material, so that the Young's modulus of the auxiliary layer **310** may be changed by adjusting the doping concentration of the inorganic material to make the Young's modulus of the auxiliary layer **310** greater than the Young's

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modulus of the hard coating layer **120**. The hard coating layer **120** may include an organic material. In other words, the auxiliary layer **310** and the hard coating layer **120** adopt the same organic material as the host material. For example, the organic materials of the auxiliary layer **310** and the hard coating layer **120** are both made of an acrylic material as a host material. The inorganic material and organic material of the auxiliary layer **310** may be similar to those described for the auxiliary layer **110** of FIG. 1A and are not repeated herein.

Referring to FIG. 3B, a protective structure **300b** is similar to the protective structure **300a** in FIG. 3A, and the difference is that the protective structure **300b** further includes the substrate **130** and the optical structure layer **140**. The auxiliary layer **310** is located at one side of the substrate **130**, and the optical structure layer **140** is located at another side of the substrate **130**. In other words, the substrate **130** is sandwiched between the auxiliary layer **310** and the optical structure layer **140**. In some other embodiments, the protective structure is similar to the protective structure **300b**, but does not include the optical structure layer **140**.

Referring to FIG. 3C, an electronic device **300c** includes the protective structure **300a** as shown in FIG. 3A and the electronic element **150**. The protective structure **300a** is located on the electronic element **150**, in other words, the auxiliary layer **310** is located between the electronic element **150** and the hard coating layer **120**.

Referring to FIG. 3D, an electronic device **300d** includes the protective structure **300b** as shown in FIG. 3B and the electronic element **150**. The protective structure **300b** is disposed on the electronic element **150**. In other words, the optical structure layer **140** is located between the electronic element **150** and the substrate **130**. The substrate **130** is sandwiched between the coating layer **120** and the electronic element **150**.

The Young's modulus of the auxiliary layer **310** of the protective structures **300a** to **300b** is greater than the Young's modulus of the hard coating layer **120**, so the electronic device **300c** having the protective structure **300a** and the electronic device **300d** having the protective structure **300b** may have improved scratch resistance and have good flexibility at the same time, and the material cracking phenomenon of the electronic devices **300c** to **300d** after folding (especially outward folding) may also be reduced, thereby increasing the service life and reliability of the electronic devices **300c** to **300d**. In addition, since the material of the auxiliary layer **310** of the protective structures **300a** to **300b** is the same as that of the hard coating layer **120**, the adhesion at the interface between the auxiliary layer **310** and the hard coating layer **120** may be improved, and the service life and reliability of the electronic devices **300c** to **300d** are further improved.

The following is an explanation of the efficacy of the protective structures of the embodiments of the disclosure via experiments and simulations.

Example 1

A stacked structure A was provided. The stacked structure A is similar to the protective structure **100b** described in FIG. 1B, but does not include the optical structure layer **140**. The forming method of the stacked structure A includes providing the substrate **130**. The substrate **130** was polyethylene terephthalate (PET) and had a thickness of 125 μm . Next, the auxiliary layer **110** and the hard coating layer **120** were formed on the substrate **130**. The forming method of

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the auxiliary layer **110** and the hard coating layer **120** includes first uniformly dispersing silicon dioxide having a concentration of 10 wt % in acrylic using a solvent. Next, a soft baking (85° C. to 105° C.) and a UV curing process were performed to volatilize the solvent in the organic material. The photocuring energy was, for example, 500 mj to 2500 mj. The formed auxiliary layer **110** was acrylic doped with silicon dioxide and having a thickness of 10 μm . From the second surface **S2** to the first surface **S1**, the concentration of silicon dioxide was 1 wt % to 10 wt %, so that the Young's modulus of the auxiliary layer **110** was gradually increased from the second surface **S2** toward the first surface **S1**. The hard coating layer **120** was an acrylic not doped with silicon dioxide and having a thickness of 10 μm . Next, the stacked structure A was subjected to a surface hardness test. The surface hardness of the stacked structure A actually measured was 7H (pencil hardness).

Comparative Example 1

A stacked structure A' was provided. The stacked structure A' is similar to the stacked structure A but does not have the auxiliary layer **110**. Hardness testing was performed on the stacked structure A'. The surface hardness of the stacked structure A' actually measured was 5H (pencil hardness).

From the results of example 1 and comparative example 1, it may be seen that the configuration of the auxiliary layer increased the hardness of the surface of the overall structure.

Example 2

A stacked structure B was provided and tested for surface hardness. The stacked structure B is similar to the protective structure **100b** described in the embodiment of FIG. 1B, that is, the stacked structure B includes the optical structure layer **140**, an adhesive layer (not shown in FIG. 1B), the substrate **130**, the auxiliary layer **110**, and the hard coating layer **120**. A polyimide phase (PI) substrate **130** having a thickness of 10 μm was provided, and then the auxiliary layer **110** and the hard coating layer **120** were formed on the substrate **130** in a manner similar to the stacked structure A. Thereafter, the optical structure layer **140** was adhered to the substrate **130** with an adhesive layer having a thickness of 2 μm . The optical structure layer **140** was a circular polarizer having a thickness of 5 to 50 μm . The auxiliary layer **110** was an acrylic material doped with silicon dioxide and having a thickness of 10 μm . The concentration of silicon dioxide was 10 wt % to 35 wt % from the second surface **S2** to the first surface **S1** such that the Young's modulus of the auxiliary layer **110** was gradually increased from the second surface **S2** toward the first surface **S1**. The formed hard coating layer **120** was an acrylic material having a thickness of 20 μm . The surface hardness of the stacked structure B actually measured was 8H (pencil hardness).

Comparative Example 2

A stacked structure B' was provided. The stacked structure B' is similar to the stacked structure B but does not have the auxiliary layer **110**. Hardness testing was performed on the stacked structure B'. The surface hardness of the stacked structure B' actually measured was 6H (pencil hardness).

From the results of example 2 and comparative example 2, it may be seen that the configuration of the auxiliary layer increased the hardness of the surface of the overall structure.

Example 3

A stacked structure C was provided. The structure of the stacked structure C is similar to the stacked structure B, and

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the difference is the doping concentration of silicon dioxide in the auxiliary layer **110**. In the stacked structure C, the concentration of silicon dioxide in the auxiliary layer **110** was 15 wt % to 30 wt % from the second surface S2 to the first surface S1. The surface hardness of the stacked structure C actually measured was 8H (pencil hardness).

Example 4

A stacked structure D was provided. The stacked structure D is similar to the stacked structure A, and the difference is that the hard coating layer **120** was an acrylic material doped with silicon dioxide. The concentration of silicon dioxide in the hard coating layer **120** was 1 wt % to 5 wt %. The surface hardness of the stacked structure C actually measured was 8H (pencil hardness).

Example 5

A stacked structure E was provided. The structure of the stacked structure E is similar to the stacked structure B, and the difference is that the hard coating layer **120** was an acrylic material doped with silicon dioxide. The concentration of silicon dioxide in the hard coating layer **120** was 1 wt % to 5 wt %. The surface hardness of the structure actually measured was 8H (pencil hardness).

Example 6

A stacked structure J was provided. The stacked structure J is similar to the protective structure **100a** described in the embodiment of FIG. 1A. That is, the stacked structure J includes the auxiliary layer **110** and the hard coating layer **120**. The hard coating layer **120** was an undoped acrylic having a thickness of 20 μm . The auxiliary layer **110** was an acrylic doped with silicon dioxide and having a thickness of 10 μm . The stacking structure J was subjected to a simulation of bending stress, and the radius of curvature was 3 mm (millimeter). The results are shown in FIG. 1E and Table 1.

The results from FIG. 1E show that the Young's modulus of the hard coating layer **120** from the top surface S3 to the bottom surface S4 is kept at a constant, that is, the Young's modulus of the hard coating layer **120** at positions with thicknesses of 30 μm , 25 μm , 20 μm , and 15 μm is always kept at 14.3 GPa. The Young's modulus at the interface of the bottom surface S4 of the hard coating layer **120** and the auxiliary layer **110** is 14.3 GPa. The Young's modulus of the auxiliary layer **110** is gradually increased from the second surface S2 toward the first surface S1. The Young's modulus of the auxiliary layer **110** at positions with thicknesses of 10 μm , 5 μm , and 0 μm is sequentially 14.3 GPa, 20 GPa, and 30 GPa.

TABLE 1

Young's modulus of hard coating layer 120 (GPa)	14.3	14.3	14.3	14.3
Young's modulus of auxiliary layer 110 (GPa)	14.3	20	25	30
Bending stress of protective structure 100a (MPa)	315.16	297.43	284.25	272.83

It may be seen from the results of Table 1 that as the Young's modulus in the auxiliary layer **110** is greater, the bending stress is gradually smaller. When the Young's modulus of the auxiliary layer **110** is 30 GPa, the bending

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stress may be reduced to 272.83 MPa (10^6 Pa), which is less than the deflection strength of 278 MPa with a deflection radius of 3 mm.

Therefore, increasing the Young's modulus of the auxiliary layer **110** reduces the bending stress received, thereby reducing the chance of deformation of the auxiliary layer **110**.

Example 7

An electronic device F was provided. The electronic device F is similar to electronic device **100d** described in the embodiment of FIG. 1D. That is, the electronic device F includes the electronic element **150**, the optical structure layer **140**, the substrate **130**, the auxiliary layer **110**, and the hard coating layer **120**. The electronic element **150** below the optical structure layer **140** includes, from top to bottom, a 12 μm optical transparent adhesive (OCA), a touch sensor, 197OCA, a thin film transistor/active matrix organic light-emitting diode (TFT/AMOLED), a 12 μm optically clear adhesive, and polyimide. The optical structure layer **140** was a circular polarizer having a thickness of 5 to 50 μm . The substrate **130** was a polyimide having a thickness of 9 to 30 μm . The auxiliary layer **110** was an acrylic material doped with silicon dioxide and having a thickness of 10 μm . The concentration of silicon dioxide was 15 wt % to 30 wt % from the second surface S2 to the first surface S1 such that the Young's modulus of the auxiliary layer **110** was gradually increased from the second surface S2 toward the first surface S1, and the hard coating layer **120** was an undoped acrylic material having a thickness of 20 μm . The surface hardness of the electronic device F was tested and the measured surface hardness was 7H (pencil hardness).

Example 8

An electronic device G was provided. The electronic device G is similar to the electronic device F of example 7, and the difference is that the hard coating layer **120** was an acrylic material doped with silicon dioxide. The concentration of silicon dioxide was 1 wt % to 5 wt % from the second surface S2 to the first surface S1. The surface hardness of the electronic device G was tested and the measured surface hardness was 7H (pencil hardness).

Example 9

An electronic device H was provided. The electronic device H is similar to electronic device **100d** described in the embodiment of FIG. 1D. That is, the electronic device H includes the electronic element **150**, the optical structure layer **140**, the substrate **130**, the auxiliary layer **110**, and the hard coating layer **120**. The electronic element **150** was an electronic element with touch function and display function (such as AMOLED). The optical structure layer **140** was a circular polarizer having a thickness of 5 μm . The substrate **130** was polyimide and a thickness of 9 to 12 μm . The substrate **130** was polyimide and had a thickness of 9 to 12 μm . The auxiliary layer **110** was an acrylic material doped with silicon dioxide and having a thickness of 10 μm . From the second surface S2 to the first surface S1, the concentration of the silicon dioxide doping was 20 wt % to 35 wt %, so that the Young's modulus of the auxiliary layer **110** was gradually increased from the second surface S2 toward the first surface S1. The hard coating layer **120** was an undoped acrylic material having a thickness of 10 μm . The electronic device H was subjected to a flexural test with a deflection

radius of 3 mm. The electronic device H passed a flexural test of folding 20,000 times outward and a flexural test of folding 20,000 times inward, showing that the electronic device H had good flexibility.

In addition, a ball drop test and a surface hardness test were further performed on the electronic device H. The steel ball weighed 135 grams and was dropped from a height of 35 cm. The electronic device H passed the ball drop test and the measured surface hardness was 7H (pencil hardness), indicating that the electronic device H had considerable hardness and impact resistance.

Example 10

An electronic device I was provided. The electronic device I is similar to the electronic device **100d** described in the embodiment of FIG. 1D. That is, the electronic device I includes the electronic element **150**, the optical structure layer **140**, the substrate **130**, the auxiliary layer **110**, and the hard coating layer **120**. The electronic element **150** was an electronic element with touch function and display function (such as AMOLED). The optical structural layer **140** was a circular polarizer having a thickness of 5 μm . The substrate **130** was polyimine and had a thickness of 9 to 12 μm . The auxiliary layer **110** was an acrylic material doped with silicon dioxide and having a thickness of 5 μm . From the second surface S2 to the first surface S1, the concentration of the silicon dioxide doping was 20 wt % to 35 wt %, so that the Young's modulus of the auxiliary layer **110** was gradually increased from the second surface S2 toward the first surface S1. The hard coating layer **120** was an undoped acrylic material having a thickness of 10 μm . A flexural test was performed on the electronic device I with a deflection radius of 3 mm. The electronic device I passed a flexural test of folding 20,000 times outward and a flexural test of folding 20,000 times inward, which shows that the electronic device I had good flexibility.

In addition, a ball drop test and a surface hardness were performed on the electronic device I. The weight of the steel ball was 135 grams and the steel ball was dropped from a height of 35 cm. The electronic device I passed the ball drop test and the measured surface hardness was 7H (pencil hardness), indicating that the electronic device I had considerable hardness and impact resistance.

Based on the above, the Young's modulus of the auxiliary layer or the hard coating layer of the protective structure of an embodiment of the disclosure is gradually increased from the second surface to the first surface, so that the electronic device having the above protective structure may have improved scratch resistance and have good flexibility, and the material cracking phenomenon of the electronic device

after folding (especially outward folding) may also be reduced, thereby increasing the service life and reliability of the electronic device.

It will be apparent to those skilled in the art that various modifications and variations may be made to the structure of the disclosed embodiments without departing from the scope or spirit of the disclosure. In view of the foregoing, it is intended that the disclosure cover modifications and variations of this disclosure provided they fall within the scope of the following claims and their equivalents.

What is claimed is:

1. A protective structure, comprising:

an auxiliary layer having a first surface and a second surface opposite to the first surface; and

a coating layer located on the second surface of the auxiliary layer, wherein the second surface of the auxiliary layer is closer to the coating layer than the first surface of the auxiliary layer, and a Young's modulus of the auxiliary layer is greater than a Young's modulus of the coating layer, and the auxiliary layer and the coating layer comprise a same host material.

2. The protective structure of claim 1, wherein the auxiliary layer comprises an organic material doped with an inorganic material, the coating layer comprises an organic material, and the organic material of the auxiliary layer is the same as the organic material of the coating layer.

3. The protective structure of claim 2, wherein the inorganic material is a nanoparticle, and the nanoparticle comprises silicon dioxide, titanium oxide, zirconium oxide, or a combination thereof.

4. The protective structure of claim 1, further comprising: a substrate disposed on the first surface of the auxiliary layer; and

an optical structure layer, wherein the substrate is located between the auxiliary layer and the optical structure layer.

5. The protective structure of claim 1, further comprising: a substrate disposed on the first surface of the auxiliary layer.

6. An electronic device, comprising:

the protective structure of claim 1; and an electronic element disposed on the first surface of the auxiliary layer.

7. An electronic device, comprising:

the protective structure of claim 1;

an electronic element; and

a substrate, wherein the substrate is sandwiched between the coating layer and the electronic element.

8. An electronic device, comprising:

the protective structure of claim 4; and

an electronic element disposed on a surface of the optical structure layer away from the substrate.

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